# Electrical Properties of ZnO doped Yttria Stabilized Zirconia.

A thesis submitted in partial fulfillment of the requirement for degree of Bachelor of Technology.


Submitted By:-

**Prateek Kumar Pujari**

**108CR003**




Department of Ceramic Engineering

National Institute of Technology, Rourkela

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Under the guidance of

**Prof (Dr). Shantanu Behera**




Department of Ceramic Engineering

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# Certificate

This is to certify that the project entitled, **"Structural and Electrical properties of ZnO doped YSZ"** submitted by **Prateek Kumar Pujari** is an authentic work carried out by him under my supervision and guidance for the partial fulfillment of the requirements for the award of **Bachelor of Technology Degree** in **Ceramic Engineering** at **National Institute of Technology, Rourkela.**

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any Degree or Diploma.

Date: - 11/05/2011

Rourkela

Prof (Dr) Shantanu Behera
Department of Ceramic Engineering
NIT Rourkela

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# Abstract

In this work, density, microstructure and electrical property were investigated on sintered samples of 8 mol % yttria stabilized zirconia and samples doped ZnO. 8 mol% yttria was used to stabilize cubic zirconia phase $\{(ZrO_2)_{0.92}\ (Y_2O_3)_{0.08}\}$ by co-precipitation method. The synthesized powders were doped with variable concentration of ZnO (0.5, 1, and 1.5 molar) by normal grinding and mixing which is followed by calcination. The Calcined powders have been pelletized by uniaxial pressing, and were sintered at different temperatures.

X-Ray diffraction was used for characterization and phase determination of samples. Scanning electron microscopy analysis was carried out to investigate the grain morphology, grain size, and pores distribution. Apparent porosity and bulk density was calculated. Finally impedance spectroscopy of sintered samples was done to determine the conductivity model, Impedance/conductivity values, and there variation with temperature. It was observed that addition of ZnO enhances the densification and promotes grain growth. Also better electrical conductivity was observed for some concentration of ZnO doping. Various conductivity models have been considered, mechanism related to densification and Grain boundary conductivity was discussed.

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# CHAPTER 1

# INTRODUCTION and OBJECTIVE

## 1.1 Introduction

Zirconia ($ZrO_2$) has a monoclinic structure at room temperature to a temperature of about 1173℃, where it changes to the tetragonal modification. For temperatures higher than 2370℃ zirconia adopts a cubic fluorite structure [1]. Aliovalent oxides such as yttria ($Y_2O_3$), calcia (CaO), or magnesia (MgO) are doped in Zirconia to stabilize more symmetric crystal structure at room temperature [2].Cubic Zirconia phase is commonly stabilized by using yttria as a dopant; a fully (cubic) stabilized zirconia is obtained with a $Y_2O_3$-content of 8 mol% [3], while a lower $Y_2O_3$ content gives a partially stabilized zirconia or tetragonal stabilized zirconia. The electronic and structural properties of a model crystal structure containing an isolated oxygen vacancy was then studied from first principles by Stapper and coworkers [4]: a cubic 96-sites supercell of 95 atoms in the fluorite structure containing one vacant oxygen lattice site, that we define as V1. The vacancy is the +2 charge (one $O^{2-}$ ion missing). In the real material, the charge of the $V^{\cdot\cdot}_O$ defect is compensated by the dopant substitutional cations $Y^{`}_{Zr.}$ The addition of substitutional cations (e.g. $Y^{3+}$), which have lower valency than zirconium ion ($Zr^{4+}$), generates oxygen vacancies for charge compensation. For example, the substitution of $Zr^{4+}$ with $Y^{3+}$ causes the vacant oxygen site in the lattice as shown in Figure 1; for every mole of yttria substituted into the zirconia lattice, the charge neutrality condition is maintained by forming a negative charge on vacant site [5]. In a Kroger-Vink notation, it is represented as follows

$$Y_2O_3 \longrightarrow 2Y'_{Zr} + 3O^x_O + V^{\cdot\cdot}_O$$

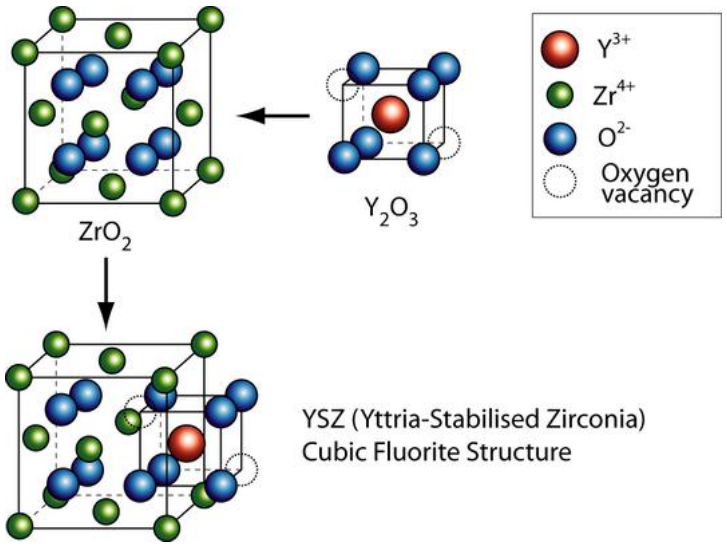


**Figure 1: Cubic Structure of Zirconia doped with Yttria.**

YSZ commonly represented as $(ZrO_2)_{0.92}$ $(Y_2O_3)_{0.08}$ is a much desired material for Solid Oxide Fuel Cell, due to the property of oxygen ion conductivity it is used as electrolyte material, high chemical and crystallographic stability [6]. The function of the electrolyte is to transport the oxygen ions from the cathode to the anode where oxidation of the fuel by the ions occurs, and also it has to block the electrons produced at the anode from passing through the cell to the cathode [7].

Operating temperature of SOFC are usually high (~1000℃), which tends to decrease the longevity of cell due to degradation in the fuel cell. In order to reduce the operating temperature, the material modification must be done in order to enhance the property to perform well under favorable conditions. It is well known that the transport properties of solid electrolytes at intermediate temperature are controlled mainly by the grain boundaries, therefore, it is possible to control and modify the electrical behavior through adding various dopants such as $CeO_2$, $Sm_2O_3$ and other transition metal oxides [8]. ZnO as dopant can be used to modify and enhance

the total conductivity; also it is expected to generate more Oxygen deficiency in the crystal structure promoting ionic conductivity at moderately low temperature [9].

## 1.2 Objective of Present work

- To prepare YSZ $\{(ZrO_2)_{0.92}\ (Y_2O_3)_{0.08}\}$ by co-precipitation process and dope it with variable concentration of ZnO.
- To sinter the doped samples and study the densification behaviour.
- Electrical characterization of the sintered ZnO doped YSZ doped and YSZ samples.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Application of YSZ in SOFC

The solid state electrolyte used in SOFCs is desired to have high ionic conductivity, better phase stability, chemical and thermal compatibility, impermeability by the reacting gases, high strength and toughness. The solid electrolyte materials mainly include fluorite-structured stabilized zirconia doped with Yttria [10-11]. Cubic stabilized zirconia ($ZrO_2$) is the most demanded electrolyte material for SOFCs. In its pure form the ionic conductivity of zirconia is low. At room temperature, zirconia has a monoclinic (m) crystal structure which transforms to a tetragonal (t) form above 1170°C and then to a cubic Fluorite form above 2370°C. However, the addition of aliovalent oxides such as $Y_2O_3$, MgO, or $Sc_2O_3$ stabilizes the cubic Fluorite structure of $ZrO_2$ from room temperature up to its melting point and, at the same time, generates oxygen deficiency in the structure, leading to enhanced ionic conductivity over an extended range of oxygen partial pressures. The creation of oxygen vacancies and stabilization of the cubic phase is accomplished by direct substitution of divalent or trivalent cations of comparable size for the host lattice cation, $Zr^{4}+$.

$$Y_2O_3 \longrightarrow 2Y'_{Zr} + 3O^{x}_{O} + V^{\cdot\cdot}_{O}$$

## 2.2 Synthesis of YSZ

A variety of methods such as spray pyrolysis, mechanical milling, and gel combustion, had been proposed for synthesis of the composite particles. However, in common sense, the process have disadvantage in production cost. Although co-precipitation is categorized in build-up process, the method can provide high quality products with lower cost than other build-up processes [12]. Thus the method is a promising candidate for production of YSZ particles. Theoretically, the method can provide fine and homogeneous material, however the grain size was still around 1 μm or more can synthesized by the method.

## 2.3 Conductivity of YSZ

The conductivity of fully stabilized zirconia as a electrolyte depends on the physical and chemical properties of the samples such as ordering, composition, porosity, grain size and ageing effects. Knowledge of the properties of grain boundaries is important because the electrolyte in the SOFC devices is frequently used in the form of polycrystalline fine-grained thin films.

According to Inozemtsev et al. [13] the grain boundary conductivity of $ZrO_2$-$Sc_20_3$ (10 mole %) increases with increasing grain size.

According **Ioffe et al**. [14] the grain boundary conductivity for $ZrO_2.Y_20_3$ (5.7 mole%) ceramics showed a linear increase of the grain boundary conductivity Ugb with the grain size dg in the region of  of the sample with a grain size of 0.2/μm is larger than expected on the basis of this linear relation.

**Inozemtsev et al**. [13] and Bernard [15] showed that the grain boundary conductivity is strongly influenced by the thermal history.

**Bernard** [15] showed that after quenching from high temperatures no contribution of the grain boundaries could be measured whereas after annealing at a lower temperature the influence of the grain boundaries was considerable.

# CHAPTER 3

# EXPERIMENTS

### 3.1 Preparation of doped and Undoped YSZ powder

Process of Co-precipitation method for synthesis of YSZ as shown in figure-2.

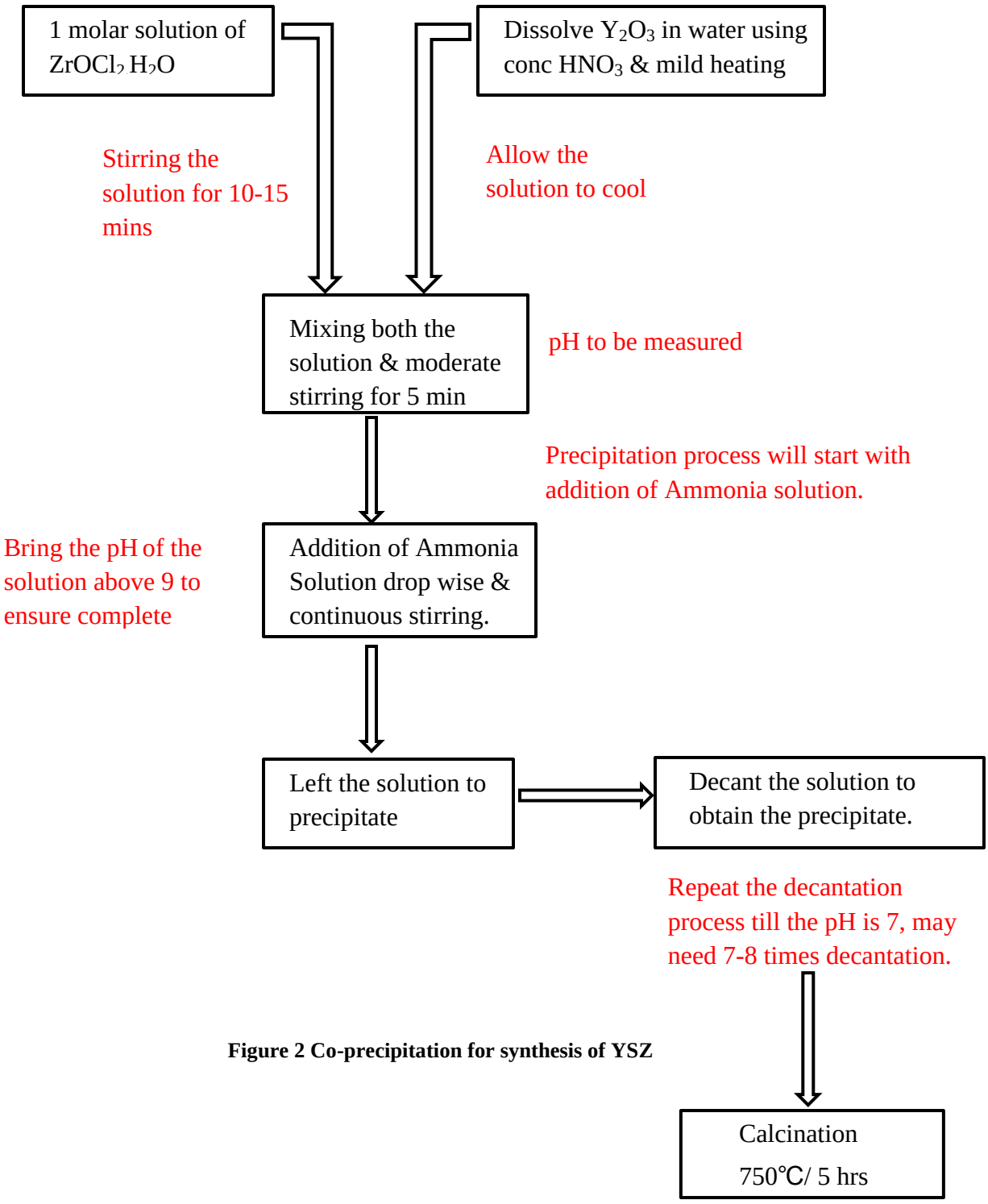


**Figure 2 Co-precipitation for synthesis of YSZ**

As discussed the YSZ was prepared by co-precipitation method. Primary precursors were $ZrOCl_2.8H_2O$ and $Y_2O_3$.

**Batch Calculation**:-

1 mol of $ZrOCl_2.8H_2O$ = 322.25gms

1 mol of $ZrO_2$ = 123.22gms

1 mol of $Y_2O_3$= 225.81gms

1 mol of $(ZrO_2)_{0.92}$ $(Y_2O_3)_{0.08}$= 131.429gms

**YSZ Batch size 5gms.**

(a) $Y_2O_3$ required in 5gms of YSZ.

131.429gms contains 18.0648gms of $Y_2O_3$.

5gms will contain 0.6872gms of $Y_2O_3$.

(b) $ZrO_2$ required in 5gms of YSZ.

131.429gm contains 113.3642gms of $ZrO_2$.

5gms contain 4.312gms of $ZrO_2$.

1 mol of $ZrO_2$ from 1 mol of $ZrOCl_2.8H_2O$.

Amount of $ZrOCl_2.8H_2O$ required for 4.312gms of $ZrO_2$= 11.2786gms

## 3.2 Pelletization and Sintering of samples

0.5g of powder was weighed for preparing pellets of each composition. The powders were mixed with few drops of poly-vinyl alcohol (PVA 3%) in an agate mortar. The powders were then pressed in a circular die of diameter 12mm at 3 ton pressure with a dwell time of 120 seconds. The pellets were then fired at 1300°C, 1400°C, 1500°C and 1650°C with a soaking time of 4 hours.

## 3.3 Density and porosity calculation

The bulk density measurement of the sintered pellets was done by calculating the dry, soaked and suspended weight after putting the pellets in vacuum for 1 hour. The bulk density is calculated by Archimedes principles and is given by the following formula:

Bulk Density = ((Dry Weight) / (Soaked Weight – Suspended Weight))*density of the liquid.

## 3.4 XRD characterization and phase determination

The XRD of the sintered Yttria Stabilized Zirconia pellets, were done using Philips X-Ray diffractometer (PW 1730, Holland) with nickel filtered Cu Kα radiation (λ = 1.5406 A° ) at 40 kV and 30mA having a scan range(°2 θ) of 15-80° at a scan speed (°2 θ/sec) of 0.04.

## 3.5 SEM and Optical Microscopy

SEM samples were polished and were subjected to ultra-sonication in Acetone then cured at 1450℃ for 15 mins. SEM analysis was carried out in JEOL-JSM 6480LV at applied generator voltage of 15 KV.

## 3.6 Impedance Spectroscopy

The sintered pellets with maximum bulk density were first coated with a silver paste and cured at 600°C for 30 minutes to provide the electric contacts. The Impedance measurement was done using a SI 1260 Solartron Impedance/Gain phase analyzer and temperature range of 300-950°C. and AC frequency range of 1Khz to 10 Mhz.

# CHAPTER 4

# RESULTS and DISCUSSION

## 4.1 Bulk density analysis at different sintering temperatures

The samples were pelletized and were fired at different temperatures ranging from 1300℃ to 1650 ℃. The change in bulk density of sample is represented in figure 3.

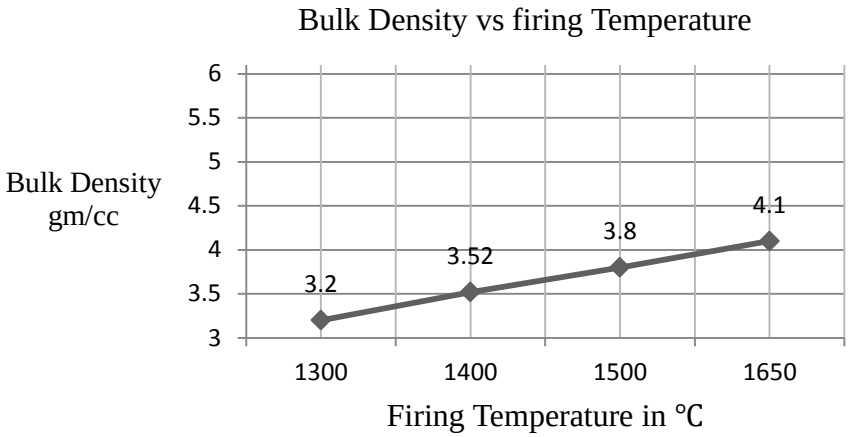


**Figure 3: Plot of Bulk density with firing temperature.**

Variation in bulk density of samples with different doping concentration of ZnO can be observed in Figure 4. All the samples were fired at 1650 ℃ for 4 hours.

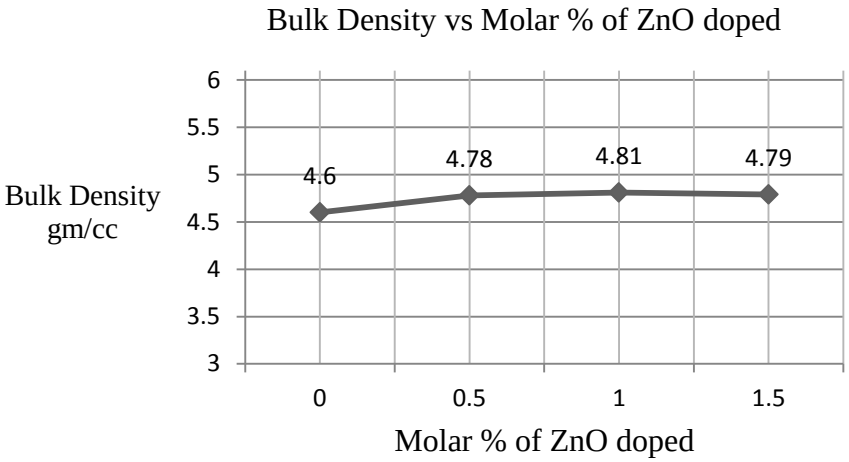


**Figure 4: Plot of Bulk density with molar % of ZnO doped in YSZ.**

## 4.2 XRD pattern of the samples

### 4.2.1 X-ray diffraction pattern of yttria stabilized zirconia.

The XRD pattern of the YSZ powder prepared by Co-precipitation method and calcined at 750℃ for 4 hour is shown in Fig-5.

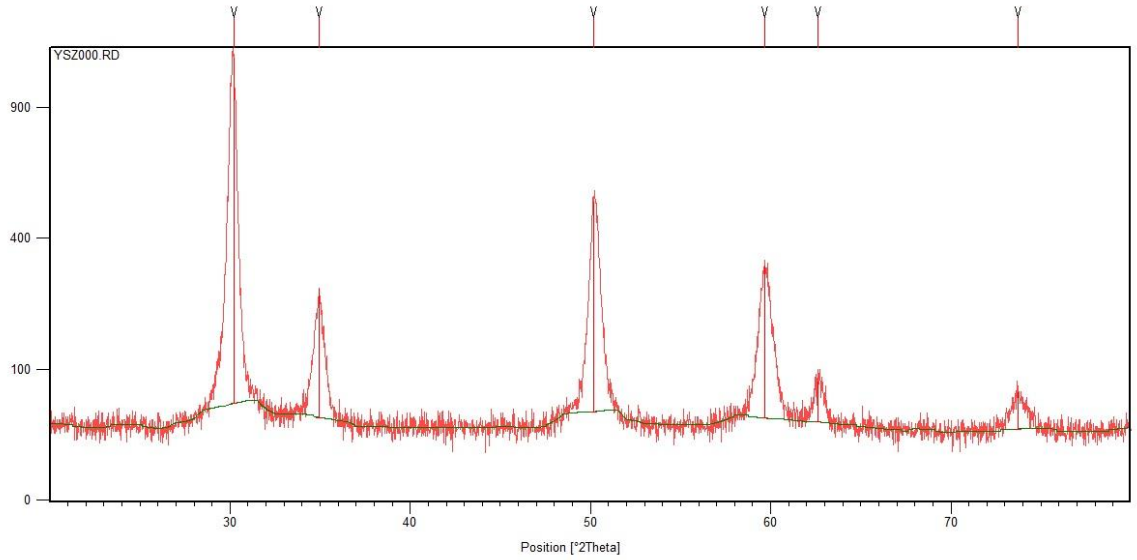


**Figure 5: XRD pattern of zirconia doped with yttria.**

The various Brags Angle and d-spacing for peaks are mentioned in Table-1.

| No. [°2Th.] | Pos. [°2Th.] Matched by | Height [cts] | FWHM [°2Th.] | d-spacing [Å] | Rel. Int. [%] | (h,k,l) |
|---|---|---|---|---|---|---|
| 1 | 30.2037 | 1087.58 | 0.2165 | 2.95905 | 100.00 | (1,1,1) |
| 2 | 34.9470 | 221.38 | 0.1181 | 2.56753 | 20.36 | (2,0,0) |
| 3 | 50.1722 | 475.02 | 0.4330 | 1.81834 | 43.68 | (2,2,0) |
| 4 | 59.6489 | 282.59 | 0.3936 | 1.55011 | 25.98 | (3,1,1) |
| 5 | 62.5983 | 46.31 | 0.3936 | 1.48398 | 4.26 | (2,2,2) |
| 6 | 73.7145 | 39.88 | 0.3840 | 1.28421 | 3.67 | (4,0,0) |

**Table 1: X-Ray analysis data for yttria stabilized zirconia .**

With reference to code 27-0997 Standard JCPDS conforms the cubic zirconia phase. Hence The XRD pattern shows that the yttria stablized zirconia synthesized through co-precipitation method.

### 4.2.2 X-Ray Diffraction pattern of yttria stabilized zirconia doped with 0.5 molar ZnO.

The XRD pattern of the YSZ doped with 0.5 molar sample synthesized by Co-precipitation method and calcined at 750℃ for 4 hour is shown in Fig-6.

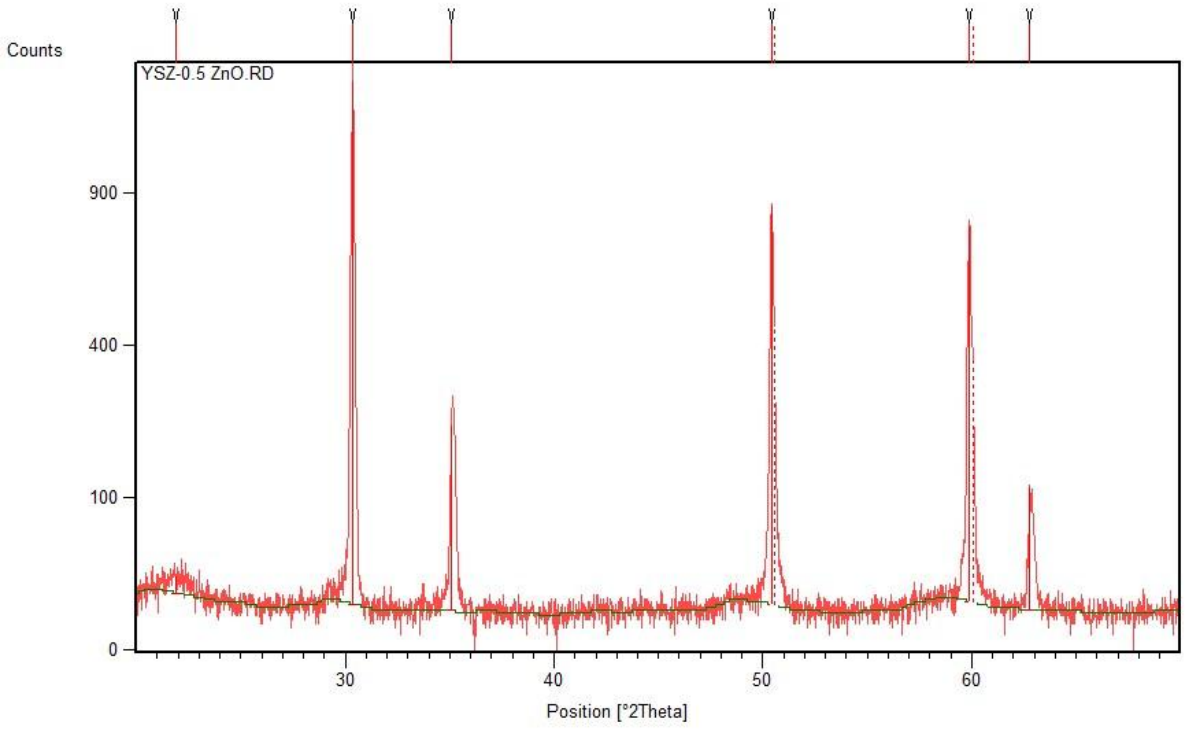


**Figure 6: XRD pattern of zirconia doped with yttria doped with 0.5 molar ZnO**

The various Brags Angle and d-spacing for peaks are mentioned in Table-2.

| No. [°2Th.] | Pos. [°2Th.] Matched by | Height [cts] | FWHM [°2Th.] | d-spacing [Å] | Rel. Int. [%] | Plane (h,k,l) |
|---|---|---|---|---|---|---|
| 1 | 21.9084 | 9.96 | 0.7872 | 4.05704 | 0.72 | (1,1,1) |
| 2 | 30.3825 | 1387.89 | 0.2165 | 2.94204 | 100.00 | (2,0,0) |
| 3 | 35.0755 | 210.94 | 0.1574 | 2.55842 | 15.20 | (2,2,0) |
| 4 | 50.4170 | 841.95 | 0.2160 | 1.80858 | 60.66 | (3,1,1) |
| 5 | 50.5644 | 445.00 | 0.0720 | 1.80814 | 32.06 | (2,2,2) |
| 6 | 59.8852 | 766.08 | 0.2160 | 1.54328 | 55.20 | (4,0,0) |
| 7 | 60.0616 | 352.26 | 0.0720 | 1.54299 | 25.38 | (3,3,1) |

**Table 2: X-Ray analysis data for yttria stabilized zirconia doped with 0.5 molar ZnO.**

With reference to code 27-0997 Standard JCPDS conforms the cubic zirconia phase. Hence The XRD pattern shows that the yttria stablized zirconia but no trace of ZnO is detected by X-Ray diffraction.

### 4.2.3 X-Ray Diffraction pattern of yttria stabilized zirconia doped with 1 molar ZnO.

The XRD pattern of the YSZ doped with 1 molar ZnO sample prepared by Co-precipitation method and calcined at 750℃ for 4 hour is shown in Fig-7.

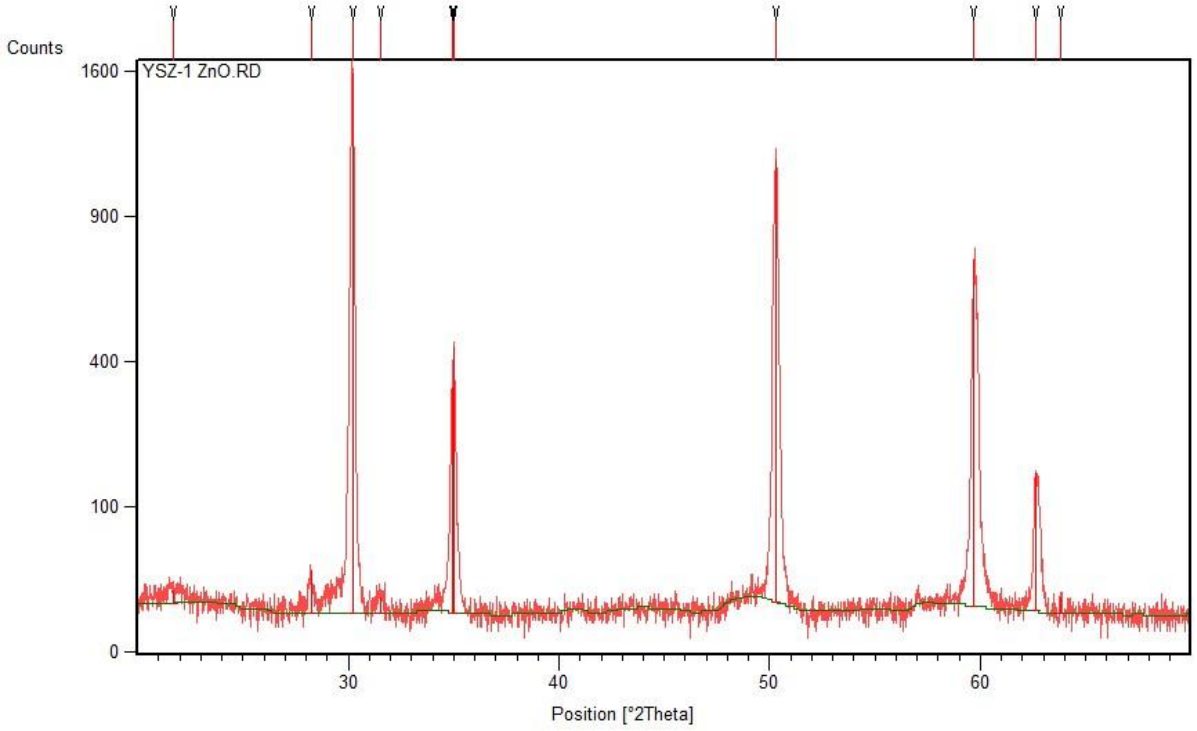


**Figure 7: XRD pattern of zirconia doped with yttria doped with 1 molar ZnO.**

The various Brags Angle and d-spacing for peaks are mentioned in Table-3.

| No [$^0$2Th] | Pos. $^0$2 Th. | Height [cts] | FWHM | d-spacing (Å) | Rel. int. (%) | Plane (h,k,l) |
|---|---|---|---|---|---|---|
| 1 | 21.7323 | 7.33 | 0.7872 | 4.08951 | 0.46 | (1,1,1) |
| 2 | 28.2516 | 24.66 | 0.2362 | 3.15891 | 1.55 | (2,0,0) |
| 3 | 30.2080 | 1586.16 | 0.2362 | 2.95864 | 100.00 | (2,2,0) |
| 4 | 31.5187 | 7.84 | 0.3149 | 2.83853 | 0.49 | (3,1,1) |
| 5 | 34.9221 | 328.77 | 0.0960 | 2.56717 | 20.73 | (2,2,2) |
| 6 | 34.9963 | 435.77 | 0.0984 | 2.56402 | 27.47 | (4,0,0) |
| 7 | 50.2779 | 1143.84 | 0.2362 | 1.81476 | 72.11 | (3,3,1) |
| 8 | 59.6930 | 719.87 | 0.1574 | 1.54907 | 45.38 | (4,2,0) |

**Table 3: X-Ray analysis data for yttria stabilized zirconia doped with 1 molar ZnO.**

With reference to code 27-0997 Standard JCPDS conforms the cubic zirconia phase. Hence The XRD pattern shows that the yttria stablized zirconia but no trace of ZnO is detected by X-Ray diffraction.

### 4.2.4 X-Ray Diffraction pattern of yttria stabilized zirconia doped with 1.5 molar ZnO.

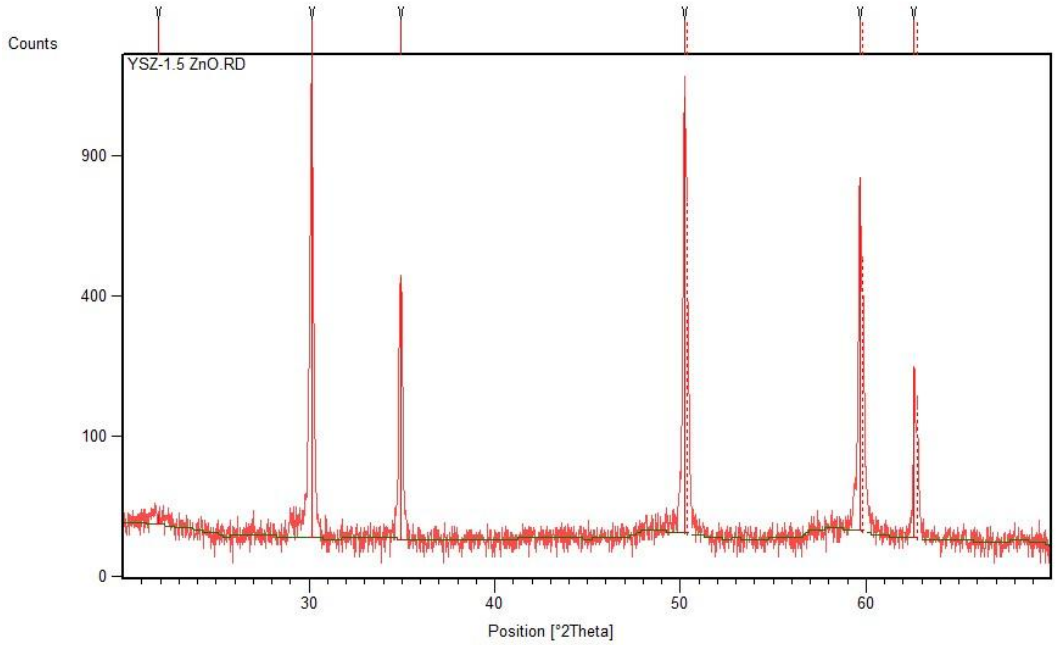


**Figure 8: XRD pattern of zirconia doped with yttria doped with 1.5 molar ZnO.**

The XRD pattern of the YSZ powder prepared by Co-precipitation method and calcined at 750℃ for 4 hour is shown in Fig-8.

The various Brags Angle and d-spacing for peaks are mentioned in Table-4.

| No [02Th] | Pos. 02 Th. | Height [cts] | FWHM | d-spacing (Å) | Rel. int. (%) | Plane (h,k,l) |
|---|---|---|---|---|---|---|
| 1 | 21.9034 | 6.05 | 0.9446 | 4.05796 | 0.43 | (1,1,1) |
| 2 | 30.1391 | 1395.38 | 0.1378 | 2.96524 | 100.00 | (2,0,0) |
| 3 | 34.9713 | 451.85 | 0.1574 | 2.56580 | 32.38 | (2,2,0) |
| 4 | 50.2119 | 1165.14 | 0.1200 | 1.81549 | 83.50 | (3,1,1) |
| 5 | 50.3510 | 708.75 | 0.0960 | 1.81529 | 50.79 | (2,2,2) |
| 6 | 59.6511 | 802.75 | 0.0960 | 1.54877 | 57.53 | (4,0,0) |
| 7 | 59.8135 | 503.22 | 0.0720 | 1.54879 | 36.06 | (3,3,1) |
| 8 | 62.5871 | 217.80 | 0.0960 | 1.48299 | 15.61 | (4,2,0) |

**Table 4: X-Ray analysis data for yttria stabilized zirconia doped with 1.5 molar ZnO.**

With reference to code 27-0997 Standard JCPDS conforms the cubic zirconia phase. Hence The XRD pattern shows that the yttria stablized zirconia but no trace of ZnO is detected by X-Ray diffraction.

## 4.2.5 X-Ray Diffraction analysis of the prepared samples

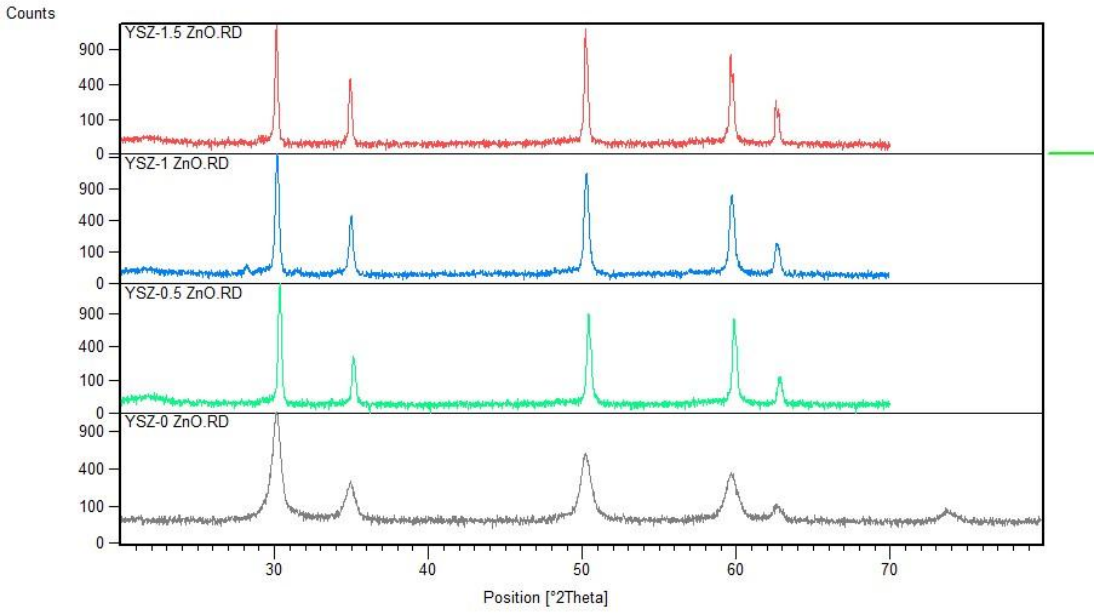


**Figure 9(a): XRD pattern of YSZ, YSZ doped with 0, 0.5, 1 and 1.5 molar ZnO.**

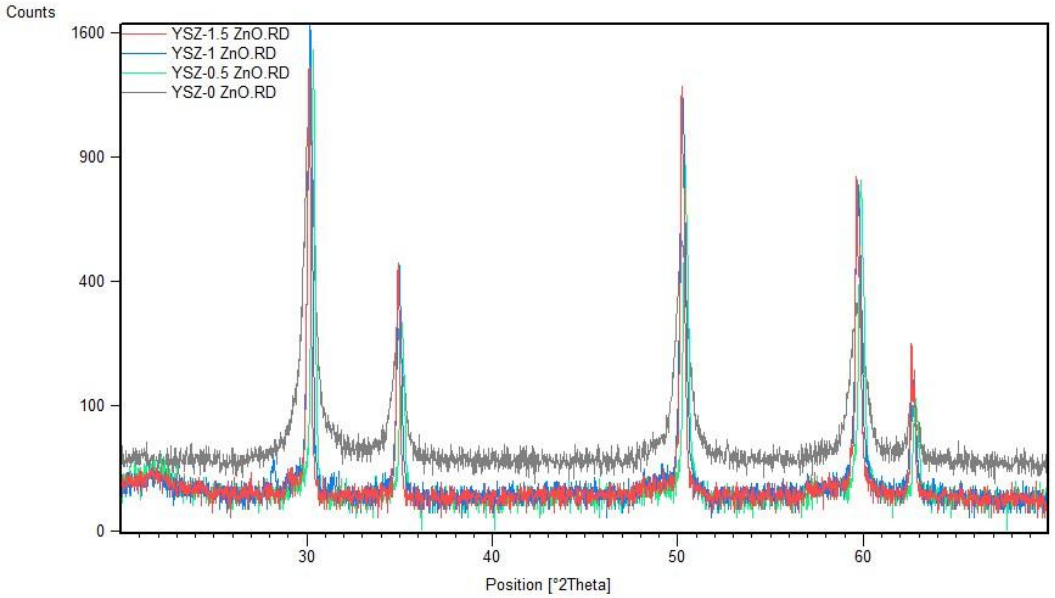


**Figure 9(b): XRD pattern of YSZ, YSZ doped with 0, 0.5, 1and 1.5 molar ZnO plotted to compare their width. .**

Analyzing all the above X-ray diffraction pattern cubic zirconia phase is conformed with reference to code 27-0997 Standard JCPDS. Hence The XRD pattern shows that the yttria stablized zirconia but no trace of ZnO is detected by X-Ray diffraction.

Also in figure 9(b) it can be observed pure YSZ samples shows a wider peak in contrast to stiffer peaks of its ZnO doped counterpart. Hence it can be inferred that grain size in doped samples is larger than undoped YSZ samples.

## 4.3 Image analysis of SEM and Optical microscopy

### 4.3.1 SEM Images of YSZ Doped with (0.5 Molar ZnO)

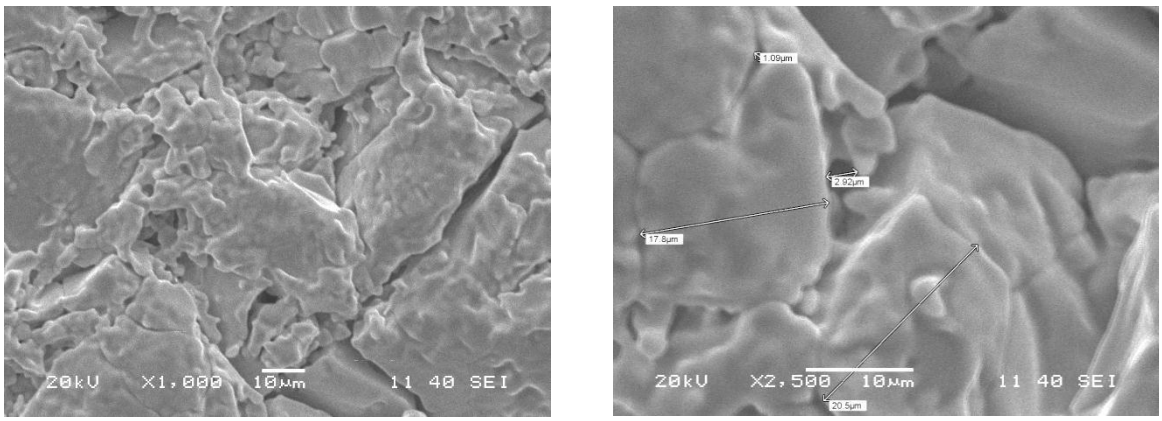


**Figure 10(a), (b): SEM of YSZ doped with 0.5 molar ZnO.**

## 4.3.2 SEM Images of YSZ Doped with (1 Molar ZnO)

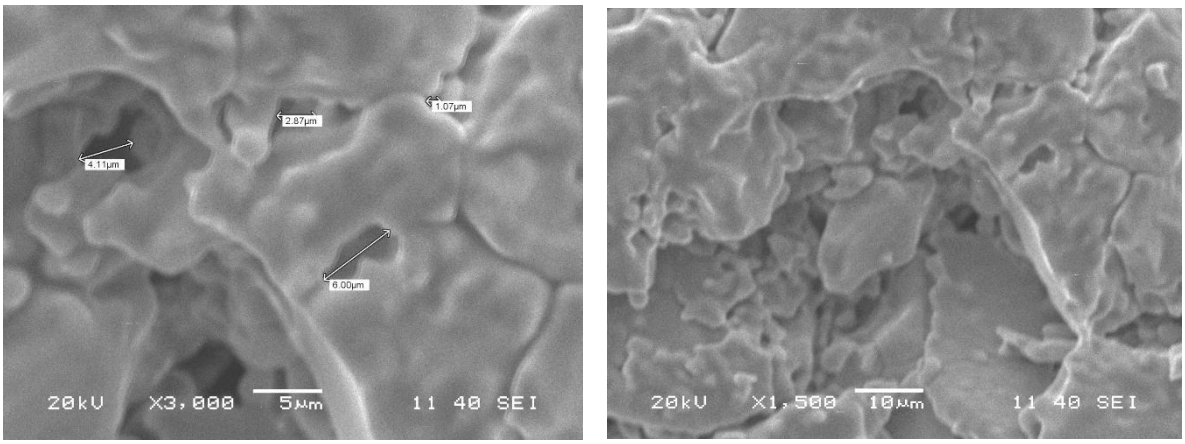


**Figure 11(a), (b): SEM of YSZ doped with 1 molar ZnO.**

## 4.3.3 SEM Images of YSZ Doped with (1.5 Molar ZnO)

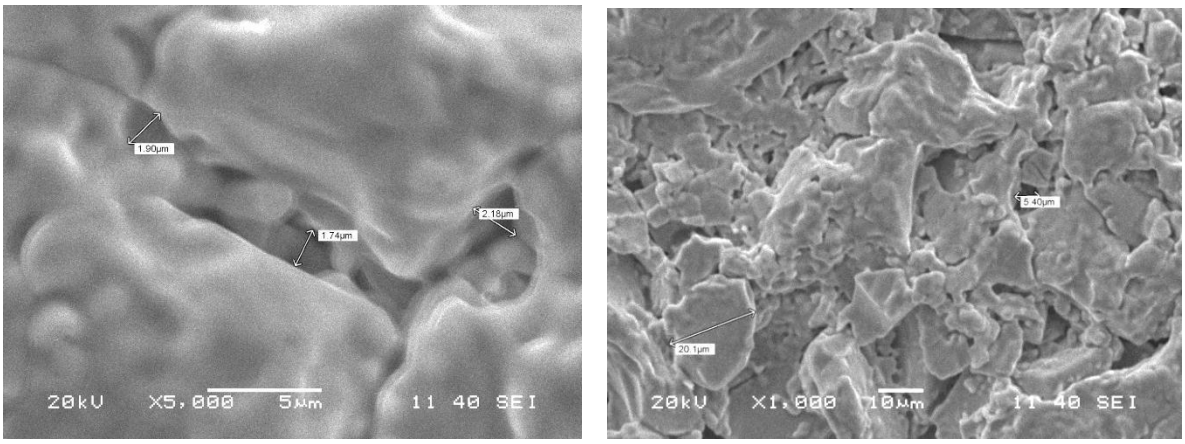


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**Figure 12(a), (b): SEM of YSZ doped with 1.5 molar ZnO.**

Average Grain Size observed for 0.5 molar ZnO doped sample was 10µm-14 µm.

Average Grain Size observed for 1 molar ZnO doped sample was 12µm-20 µm.

Average Grain Size observed for 1.5 molar ZnO doped sample was 13µm-14 µm.

## Impedance Spectroscopy

The variation of |Z| with temperature at 25Khz and 50 Khz AC frequency for samples doped with 0.5, 1, and 1.5 molar ZnO is represented in Figure 11(a), (b).

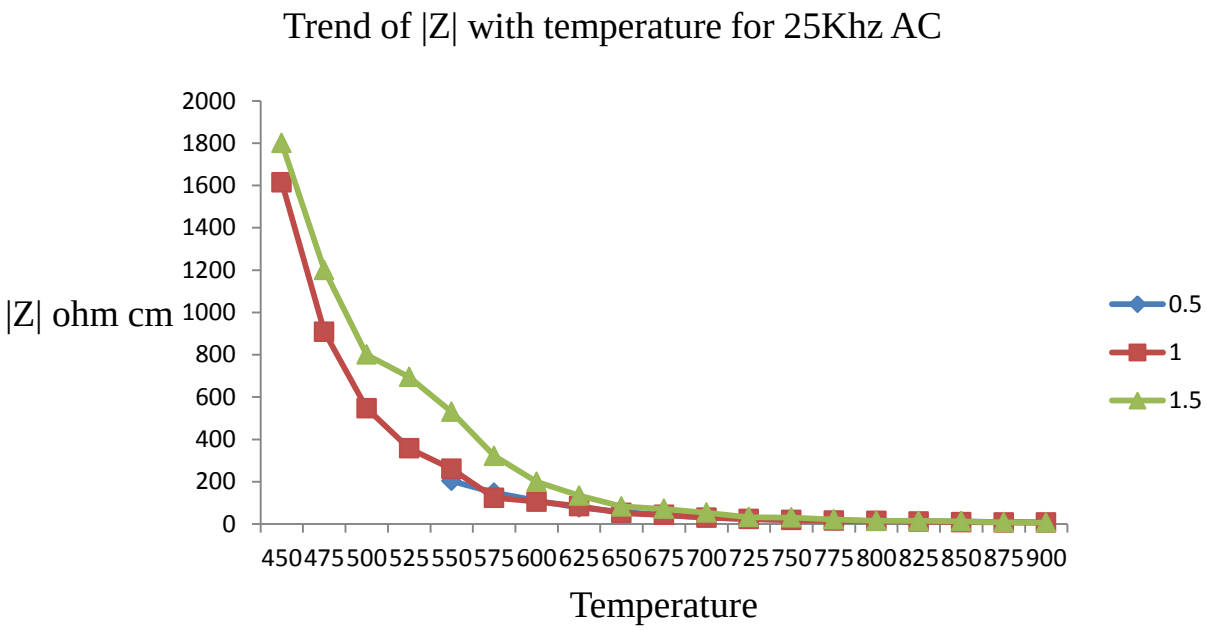


**Figure 13(a): Variation of |Z| with temperature for 25Khz for YSZ samples doped with 0.5, 1, 1.5 molar ZnO.**

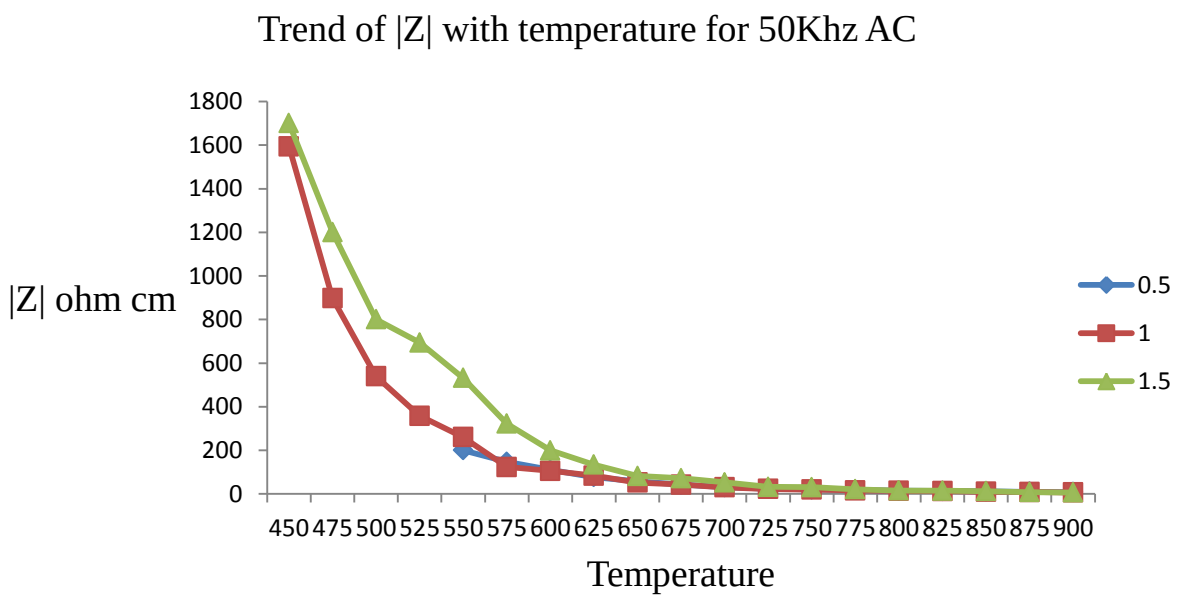


**Figure 13 (b): Variation of |Z| with temperature 50khz for YSZ samples doped with 0.5, 1, 1.5 molar ZnO.**

The variation of |Z| with AC frequency at temperature 700℃ for samples doped with 0.5, 1, and 1.5 molar ZnO is represented in Figure 13(a), (b).

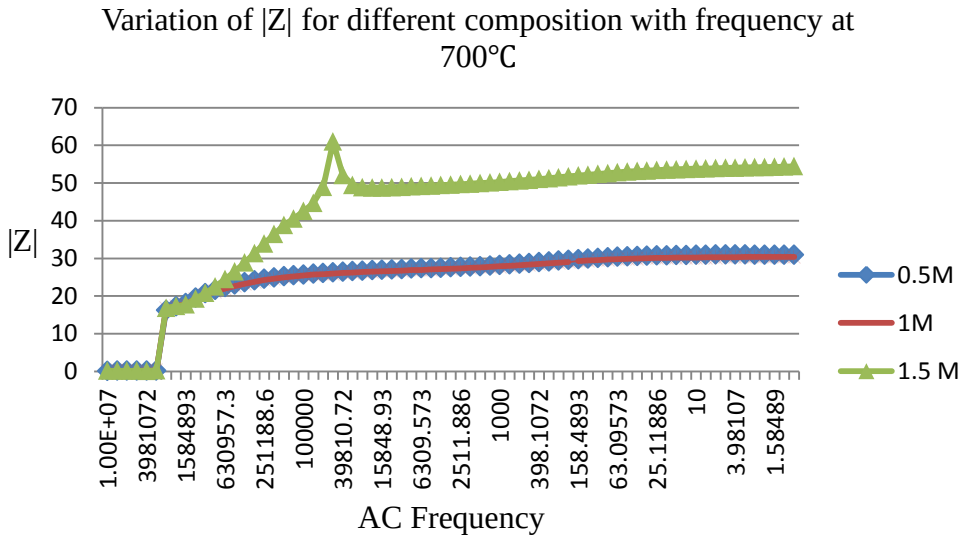


**Figure 14: Variation of |Z| with Frequency at 700℃ for YSZ samples doped with 0.5, 1, 1.5 molar ZnO.**

The plot between Z`` and Z` at temperature 450℃, 525℃, 650℃, 750℃ and 850℃ for samples doped 1 molar ZnO is represented in Figure 13(a), (b), (c), (d) and (e).

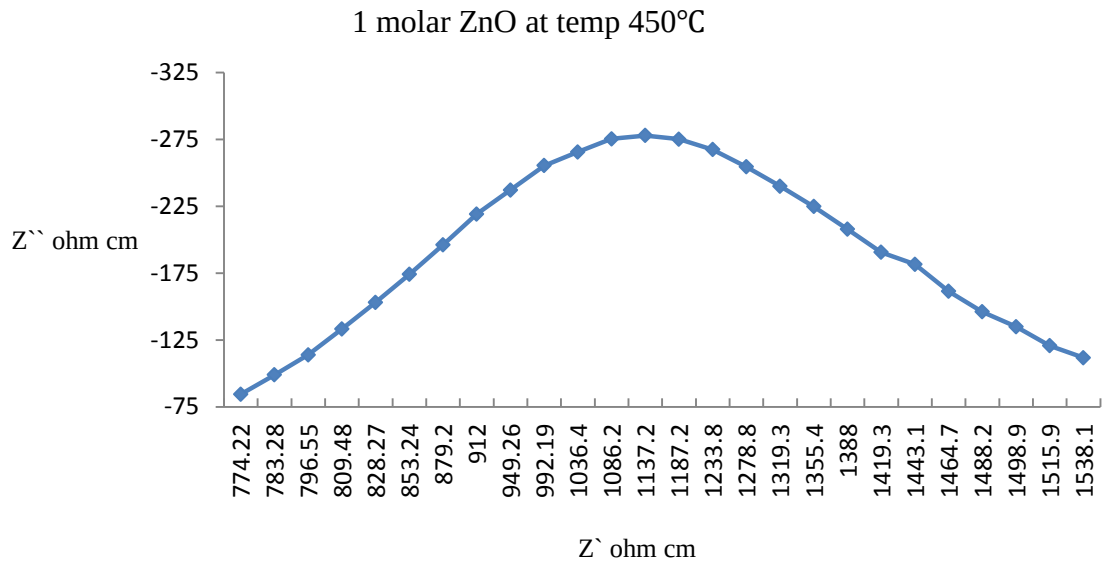


**Figure 15(a) : Plot of Z`` and Z` at 450 for YSZ sample doped with 1 molar ZnO.**

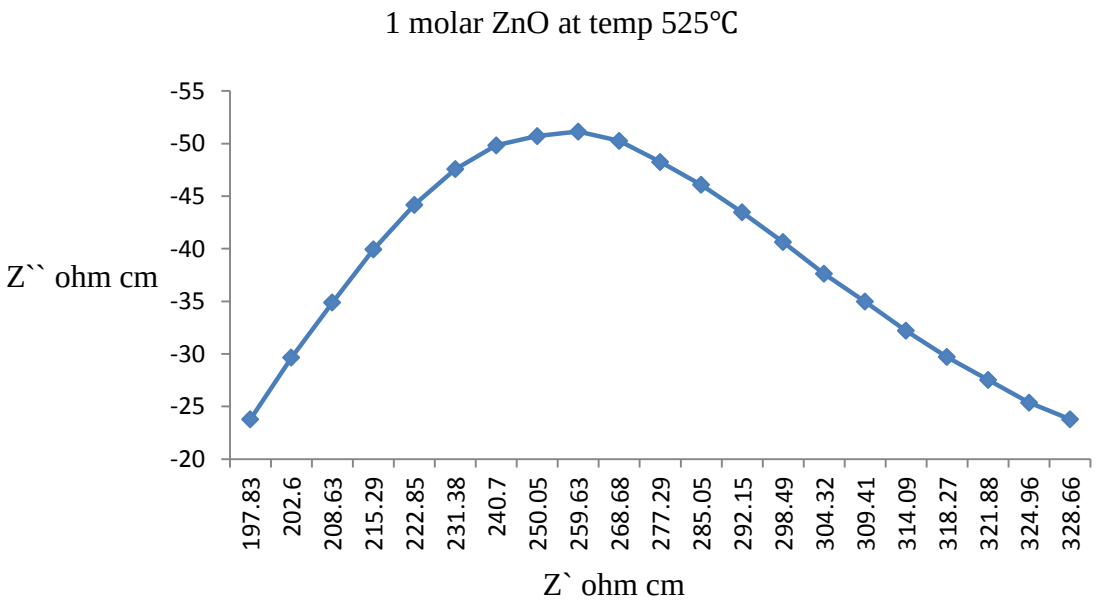


**Figure 15 (b): Plot of Z`` and Z` at 525℃ for YSZ sample doped with 1 molar ZnO.**

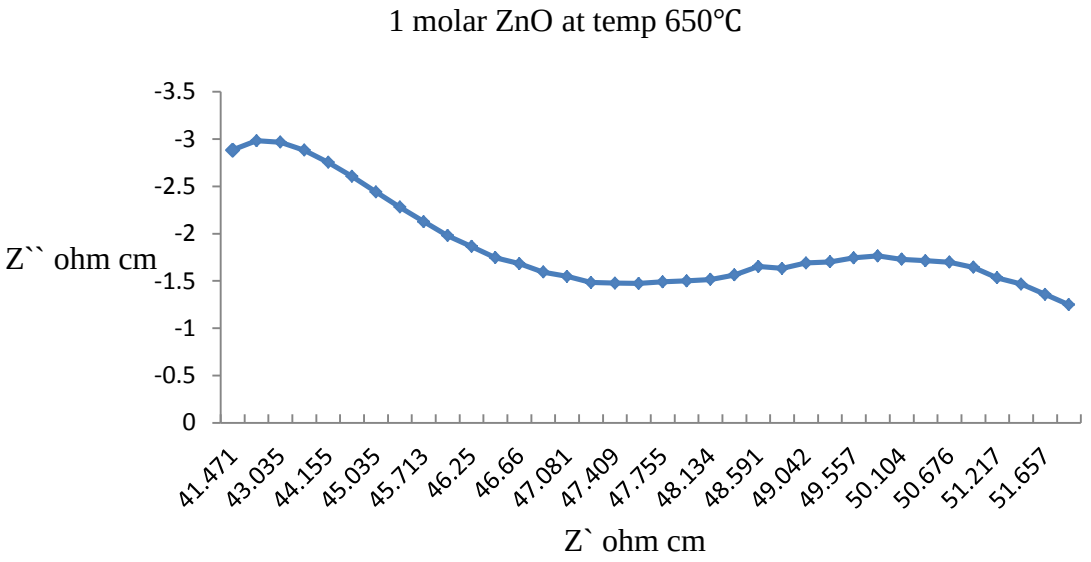


**Figure 15 (c): Plot of Z`` and Z` at 650℃ for YSZ sample doped with 1 molar ZnO.**

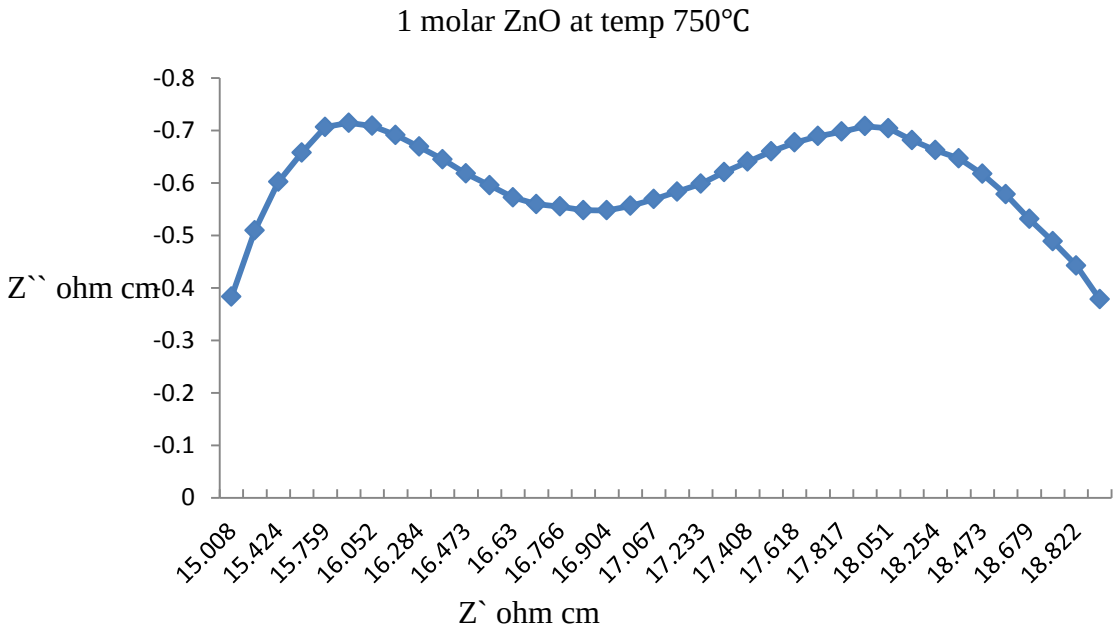


**Figure 15 (d): Plot of Z`` and Z` at 750℃ for YSZ sample doped with 1 molar ZnO.**

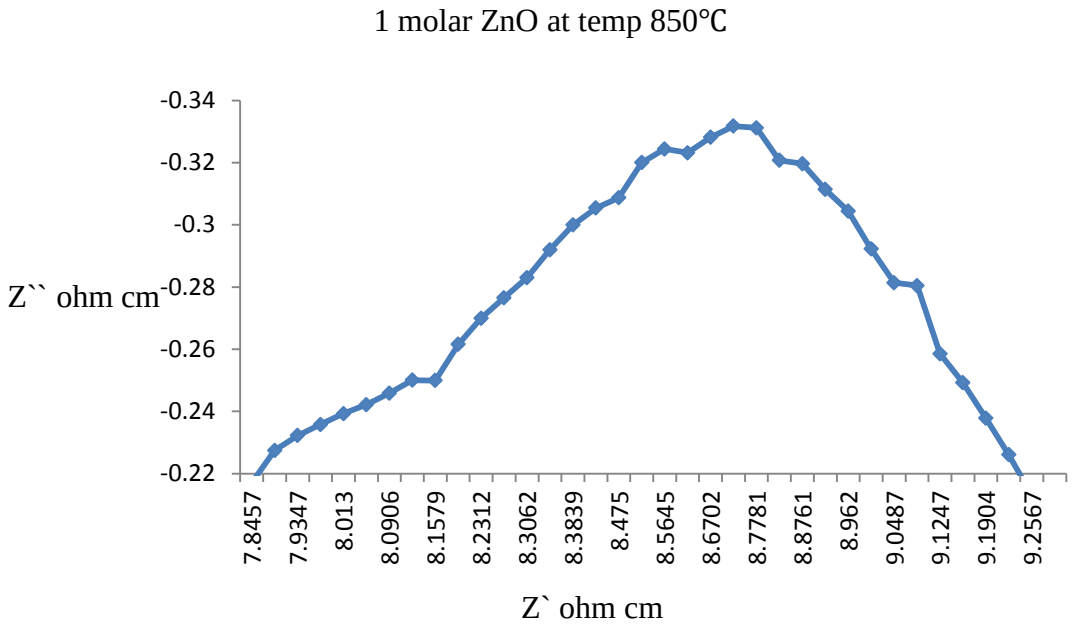


**Figure 15 (e) : Plot of Z`` and Z` at 850℃ for YSZ sample doped with 1 molar ZnO.**

# CHAPTER 5

# CONCLUSION

## Conclusion

From the above experimental data we can conclude that:-

1. ZnO was found to enhance the Ionic conductivity of $ZrO_2$ presumably by generating oxygen deficiency in the structure.
2. Lesser density of samples is due to agglomeration of particles during Co-precipitation synthesis. It was also found that ZnO increases the grain growth kinetics of $ZrO_2$. However, no parametric evaluation of grain growth was carried out. Therefore it is difficult to quantify the said effect from the current set of experiments.
3. Impedance value is very much dependent on the density of the samples, samples were found to have relatively lower density as compared to similar condition of sintering this may be ascribed to the non-uniformity of processed powder, agglomerates formed.
4. Also it is observed that Ionic conductivity of YSZ sample doped with 1molar ZnO was better ionic conductivity that other doped and undoped samples.

# CHAPTER 6

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